N64-33918

(ACCESSION NUMBER)

(FAGRS)

(CODE)

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

FIRST QUARTERLY REPORT

ON

RESEARCH AND DEVELOPMENT ON CELLS WITH BELLOWS CONTROLLED ELECTROLYTE LEVELS

(June 10, 1964 to September 10, 1964)

CONTRACT NAS5-3813

Prepared By:

THE ELECTRIC STORAGE BATTERY COMPANY MISSILE BATTERY DIVISION RALEIGH, NORTH CAROLINA

FOR THE

GODDARD SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GREENBELT, MARYLAND

XEROX \$ 2, C

FIRST QUARTERLY REPORT

ON

RESEARCH AND DEVELOPMENT ON CELLS WITH BELLOWS CONTROLLED ELECTROLYTE LEVELS (June 10, 1964 to September 10, 1964)

CONTRACT NASS-3813

Prepared By:

THE ELECTRIC STORAGE BATTERY COMPANY MISSILE BATTERY DIVISION RALEIGH, NORTH CAROLINA

F. S. Cushing

Project Engineer

A. M. Chreitzberg

Assistant Director of Engineering

Approved By

G. S. Hartman

Director of Engineering

SUMMARY

33918

Preliminary Cd/KOH/NiOOH cell tests have verified that bellows action in a sealed cell can be used to flood the plates under low pressure conditions to maximize discharge capacity and to drain the plates under high pressure overcharge conditions to aid in gas recombination.

A prime problem area is shown to be the low rate of recombination of $\mathbf{0}_2$ gas at the negative Cd plates which remain much too wet after simple drainage of electrolyte from the cell pack into the space offered by the contracting bellows device.

A survey of commercially available metal bellows revealed that the ratio ($\Delta V/V$) of the volume change (ΔV) between conditions of maximum extension (lowest pressure) and maximum contraction (highest pressure) to the rectangular volume (V) required for installation in a sealed cell does not now exceed 0.4. Plastic pillows, partially inflated with air, and sealed within the cell are proposed as bellows substitutes. The pillow $\Delta V/V$ value is approximately twice the present bellows volume efficiency.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	ii
TABLE OF CONTENTS	iii
LIST OF ILLUSTRATIONS	iv
LIST OF TABLES	v
INTRODUCTION AND SCOPE	1-2
DISCUSSION OF WORK IN PROGRESS	2-13
NEW TECHNOLOGY	13
PROGRAM FOR NEXT QUARTER	13-14
CONCLUSIONS AND RECOMMENDATIONS	14-15
BIBLIOGRAPHY	16-17

LIST OF ILLUSTRATIONS

			Page
Figure	1 -	Typical Bellows Installations in Sealed Cells	18
Figure	2 -	Experimental Nickel-Cadmium Cell 6.0 AH Plate Group	19
Figure	3 -	Electrolyte Level Variation During Charge of Sealed 15 AH Ag-Cd Cells	20

LIST OF TABLES

			<u>Page</u>
TABLE	I	Effect of Electrolyte Content on 2-Hour Rate Discharge Capacity of Sintered Plate Nickel- Cadmium Cell with Microporous PVC Separators	21
TABLE	II	Relative Capillary Properties of Separator Materials	22
TABLE	III	Cell Separator Drain Tests	23
TABLE	īV	Characteristics and Estimated Performances of Commercial Metal Bellows	24-25
TABLE	V	Electrolyte Level Variation In 4 AH Ni-Cd Cell Containing Polyethylene Pillows With Externally Imposed Pressure Changes	26
TABLE	IV	Electrolyte Level Variation During Charge and Open-Circuit of 4 AH Cell With Double Nylon Cloth Separators and Pillows	
TABLE	VII	Concentration and Level Changes in Electrolyte During Charge and Discharge	28
TABLE	VIII	Electrolyte Level Changes Observed in Sealed Ag-Cd Cells During Charge and Discharge	29

1. Introduction and Scope. -

The Electric Storage Battery Company, Missile Battery Division, Raleigh, N. C. was awarded a contract 10 June 1964 by the National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Maryland, to investigate the feasibility of controlling electrolyte levels in cycling sealed Cd/KOH/NiOOH, Cd/KOH/AgO, and Zn/KOH/AgO cells with a bellows assembly installed in each cell. The purpose of the automatic electrolyte level control feature in each cell is to create a desirably high electrolyte level for discharging cells in a flooded element condition and a desirably low electrolyte level for overcharging in a starved electrolyte condition to maximize both discharge capacity and overcharge gas recombination rates.

Previous experimental data has shown that "starved electrolyte" conditions in a sealed cell, while ideal for the recombination of gases generated during overcharge, lead to capacity losses at high rates of discharge up to 50% of the discharge capacity obtained under flooded element conditions.

The contract (1) specifies the following investigations:

- Task 1 Feasibility of a Bellows Controlled Electrolyte

 Level in Sealed Cd/KOH/NiOOH Cells.
- Task 2 Feasibility of a Bellows Controlled Electrolyte

 Level in Sealed Cd/KOH/AgO and Zn/KOH/AgO Cells.
- Task 3 Feasibility of a Charge Cutoff Switch Actuated by a Bellows Within a Sealed Cd/KOH/NiOOH or Cd/KOH/AgO Cell.

Task 4 - Production of Sealed Cd/KOH/AgO Cells

Incorporating an Optimized Bellows Design.

During the first quarter, preliminary cell tests on Cd/KOH/NiOOH cells and Cd/KOH/AgO cells have been completed to determine the critical bellows performance characteristics, and a survey of commercially available bellows, or substitutes, has been made.

2. Work Accomplished During First Quarter. -

- 2.1 <u>Feasibility Study of Electrolyte Level Controlled By Bellows</u> in a Sealed Cd/KOH/NiOOH Cell. -
- 2.1.1 <u>Literature Survey</u>. U.S. Patent 2,131,592 awarded 27 September 1938 to Lange, Langguth, Breuning, and Dassler describes the basic idea for incorporating an expansion chamber in lead acid batteries and in alkaline nickel cadmium batteries to lower electrolyte levels during open-circuit stand and during discharge by accumulating gas pressure to accelerate the recombination of gases in sealed cells. The various types of expansion chambers described in this patent consisted of air compartments adjacent to or surrounding the principle cell cavity, a sealed bellows within an air compartment, a piston actuated by a spring and trapped air, and an air compartment containing a closed cell rubber Each system was dependent upon operation in an upright orientation and provided vent plugs for venting the cell compartment to the atmosphere during charge to restore the electrolyte level to the original one atmosphere level. Similarly, U.S. Patent 2,614,138 awarded 14 October 1952 to P.A.C. Jacquier, describes variations of electrolyte expansion chambers, some of which provide gas chambers reached only by diffusion through a porous cathode barrier.

No application of the bellows in a permanently sealed cell was found in the literature survey.

- 2.1.2 Conferences During The Quarter. -
- 2.1.2.1 <u>First Conference</u>, <u>June 4</u>, <u>1964</u>. Mr. T. Hennigan (NASA, GSFC) met with MBD representatives A. M. Chreitzberg and F. S. Cushing at Raleigh, North Carolina to coordinate the planning of cell tests on the contract.
- 2.1.2.2 <u>Second Conference</u>, <u>September 9</u>, <u>1964</u>. Mr. K. Sizemore (NASA, GSFC) met with MBD representatives A. M. Chreitzberg and F. S. Cushing at Raleigh, North Carolina to discuss contract progress.
- 2.1.3 <u>Preliminary Cell Tests.</u> Two 4 AH sintered plate Ni-Cd cells were employed to observe the effect of electrolyte level on discharge performance required of a bellows to drop the electrolyte level from the flooded condition to the "electrolyte starved" condition. It was agreed at the conference of June 4, 1964, to test the cells under the following conditions:
 - a. Electrolyte levels of full, 2/3 full, 1/3 full, and drained.
 - b. Discharge capacity test at a discharge rate of C/2 (2.0 amps) to a 1.00 volts per cell voltage cutoff.
 - c. Charge to 140% of rated capacity (4.0 AH), or a maximum cell pressure of 50 psig.
 - d. Charge and overcharge to be a constant current of C/10 (0.40) amps.

Table I lists the experimental results obtained during 12 test cycles on each of the two cells. The two cells contained elements assembled in 1962. One cell was stored sealed and dry while the other was activated, cycled 2 to 3 full cycles, and then stored wet discharged for two years. The order of the tests in Table I was randomized to eliminate any effect

of the prior history. Under the conditions of these preliminary tests, no capacity increase was found when the electrolyte level was raised from fully drained to flooded levels.

The failure to find an electrolyte level effect on capacity is attributed to having the discharge rate too low for tests at room temperature and to having too much electrolyte even in the cells representing a fully drained condition. Table I lists the measured electrolyte weights of 31% KOH electrolyte observed after simple draining operations to the desired equilibrium levels. In the forced drain condition the cell was over-discharged and gassed to force more electrolyte out of the cell element assembly. Even in the forced drain condition, with little or no residual electrolyte available for flow into a bellows cavity, the electrolyte volume did not limit cell performance under the test conditions.

- 2.1.4 <u>Selection of Separator System</u>. It seems clear that for bellows controlled electrolyte level operation, a separator should be selected to have the following characteristics:
 - a. Retention of sufficient electrolyte, when fully drained, to permit the necessary rates of ionic and gas transfer for normal discharge rates and for rapid oxygen recombination at the negative plate.
 - Capability for rapid drainage rates for prompt establishment of recombination reactions at the initiation of overcharge; and,
 - c. Resistance to chemical attack by caustic and dissolved oxidants in the cell and maintenance of desirable physical properties during cycle life.

It would be desirable to select an absorber material with low absorbency and low wicking capacity such as a coarse weave nylon to promote drainage. An alternate approach would be to wind small diameter smooth monofilament plastic strands vertically against the positive plates to form intermittent parallel drain channels beneath a surrounding partially wetted absorbent material. Simple lattice work spacers such as screening or diamond hole netting are also worthy of consideration. Prior work at MBD created a need to evaluate the wicking capabilities of commercially available separator system absorbers. The test devised consisted of a 1.0" wide x 10" long strip of the absorber hung dry vertically above and dipping into a shallow dish of battery electrolyte. capillary rise of electrolyte in the strip of absorber against opposing gravitational force was observed versus time. Table II contrasts the relative wicking capabilities and absorbency of common separator materials. Table III contrasts relative drainage rates in simple drain tests at "1" g.

Filaments improve rates of drainage of "free" electrolyte but do not reduce the amount of liquid retained by Pormax and nylon cloth. Filaments would, however, provide flow channels for free electrolyte expelled by gassing forces in an overcharging element.

Screening and net materials allow relatively high degrees of drainage in a short period, and surprisingly show liquid retention values per square inch after two minutes drain comparable to Pormax and nylon cloth. Proper selection of separator materials will be facilitated by use of standard (4) (5) (6) screening methods and previous evaluation programs.

2.1.5 Survey of Commercial Bellows. - Eleven companies advertising

commercially available metal and plastic bellows were contacted for engineering information on bellows characteristics. Calculations of the volume V required to install such bellows in 6 AH Ni-Cd cell soon showed that the volume occupied by a bellows assembly might exceed the volume occupied by the cell unless exceptionally efficient bellows nesting designs were used. Assuming a bellows volume change $-\Delta V$ (fully extended volume less fully nested volume) of 20 cc for a cell internal pressure change $+\Delta P$ (maximum pressure during overcharge less minimum pressure after discharge), characteristic values of $\Delta V/V$ were calculated for the optimum bellows designs. So far the <u>best</u> range of $\Delta V/V$ found for commercially available bellows is 0.3 to 0.4, or an installation volume range (for a $\Delta V = 20$ cc) of 50 to 67 cc to be added to the proposed 6.0 AH normal test cell volume of 127 cc.

Table IV summarizes the physical characteristics of the optimum bellows designs found to date, of one typically inefficient design and lists the calculated $\Delta V/V$ constants. Figure 1 is a sketch of possible methods for the installation of bellows or bellows substitutes in a sealed cell. Figures 1A and 1B show one bellows per cell with internal or external actuation during overcharge high pressure and after discharge low pressure conditions. Figure 1C shows the similarity to a bellows of an air chamber vented to the cell cavity. Figure 1D shows the bellows replaced by heat sealed, partially inflated plastic pillows. All devices operate in essentially the same fashion and are dependent upon high gas pressures at the end of overcharge lowering electrolyte levels by compressing air in some form of entrapment; i.e. bellows, pillow, or air chamber. Each design is position dependent. Bellows are available now at reasonable

prices only in cylindrical designs and would be inefficient in rectangular cavities. The plastic pillows have varying permeabilities to gases encountered in sealed cells, yet have ideally high values of $\Delta V/V$. Each approach has its own set of engineering problems.

2.1.6 <u>Test Cell With Polyethylene Pillows</u>. - To determine the feasibility of the sealed pillow air cavity as a simple substitute for a bellows, a 4.0 AH nickel-cadmium cell was equipped with two pillows fabricated by heat sealing two sheets of 4 mil stock polyethylene. The ideal gas law was used to calculate the volume of air to be sealed in each pillow so that under an absolute pressure change of 0.33 atm to 4.4 atm the test plate pack would change from a well drained to a flooded condition.

Table V summarizes the observed variation in cell electrolyte level as the cell pressure was changed with an outside vacuum pump or air pressure source. Drainage kept pace with pressure changes when a single layer of 116 x 116 mesh nylon cloth was used as the interplate separator.

When a similar cell with a double layer of nylon cloth separation was discharged, the cell pressure adjusted to 0.1 atm, with a vacuum pump and then charged in the sealed condition into overcharge, the electrolyte level was observed to drop from 74% of plate height to below the bottom of the plates as expected. The charge was interrupted at an absolute cell pressure of 1.2 atm to observe the rate of decay of pressure by recombination reactions. After an open-circuit stand of 29 hours the recombination was still incomplete with the electrolyte level remaining 3% below the initial level of 74% plate height.

A continuation of C/10 overcharge for 15.5 hours raised the cell absolute pressure to 3.2 atm and dropped the electrolyte level below plate bottoms again. After a second open-circuit period of 120 hours duration, the cell pressure had subsided to the "initial" condition of 0.1 atm and the electrolyte level returned to its maximum height of 74% plate immersion. Recharge at the C/10 rate after discharge at the C/2 rate again lowered the cell electrolyte level from 74% plate immersion to zero percent immersion. The pressure change required was an increase in pressure from 0.1 atm to 1.24 atm, which compares favorably with the $\pm \Delta P$ value of 1.10 atm observed on the initial charge. The data observed are summarized in Table VI.

The preliminary observations thus indicate that spontaneous pressure changes in a sealed Ni-Cd cell can influence electrolyte level in the same manner that manually controlled pressure changes in the cell do. This experiment confirmed the feasibility of bellows operation in a long duration orbit and demonstrated the improved volume efficiency of the plastic pillow over the metal bellows. The fully compressed pillow volume was 4 to 6 cc in this cell. The fully expanded pillow volume was 23 cc, giving a calculated $\Delta V/V$ of 0.74 which is approximately twice the volume efficiency of the best metal bellows found to date.

This experiment also confirmed that bellows operation in the normal satellite orbit of 90 minutes will be difficult because the restoration of low pressures does not occur promptly. Recombination occurs much too slowly because of excessive wetting of the negative plates.

(7) (8)(9)
Thomas and others analyzed oxygen consumption rates on opencircuit and found that pressure decay is governed by the expression:

$$\ln \frac{Po}{P} = \frac{RT \text{ ASD}}{V \delta} \cdot t$$

where R is the gas constant, T the absolute temperature, A the effective negative plate surface area available for 0_2 consumption, S the solubility of 0_2 in the cell electrolyte at one atmosphere 0_2 partial pressure, D the diffusion coefficient, V the gas volume in the cell, δ the effective thickness of the diffusion layer, and t the time elapsed between the initial high pressure Po and the final pressure P.

To improve recombination rates the above expression predicts success for four approaches:

- a. Increase negative plate area A available for recombination;
- b. Increase the solubility of 0₂ in electrolyte by decreasing the concentration of electrolyte;
- c. Decrease the volume of 0_2 in the cell by decreasing the free space around and above the cell pack; and
- d. Decrease the effective thickness of the layer of electrolyte on the negative plate.

Quantitatively, the effect of decreasing the concentration of KOH from 31% to 25% would be to approximately double the $\mathbf{0}_2$ solubility and the recombination rate. A hundredfold increase in recombination rate is needed to make bellows operations feasible in a 90 minute orbit cycling routine. A decrease in gas volume V coupled with a major change in electrolyte content per cell and a well selected absorber separator material are most likely to

create a combined order of magnitude increase in $\mathbf{0}_2$ recombination.

- 2.1.7 <u>Six Ampere-Hour Test Cells.</u> To test the predictions of recombination theory, a group of fifteen 6-ampere-hour test cells will be constructed during the next quarter. Sintered plates 0.050ⁿ thick have been manufactured at the Nickel-Alkaline Battery Division, West Orange, New Jersey, and were shipped to MBD during September 1964. Figure 2 illustrates the arrangement of the six positive-seven negative plate pack. Each cell will be assembled with a pressure gauge and a safety pressure relief valve in prefabricated Lucite jars with the designated test bellows design.
- 3. Feasibility of a Bellows Controlled Electrolyte Level in Sealed Cd/KOH/AgO and Zn/KOH/AgO Cells. -
- 3.1 <u>Introduction</u>. Compared to the cell system Cd/KOH/NiOOH which has no semi-permeable membrane, the cell systems silver oxide-cadmium and silver oxide-zinc require a semi-permeable membrane to filter out and to react with suspended or dissolved silver-oxides which can discharge the negative electrode chemically. In addition, the semi-permeable membrane must prevent zinc dendrites or cadmium moss from growing between negative and positive plates on charge and creating cell electrical shorts.

The inclusion of the semi-permeable membrane in the cell design creates by osmotic effects a new cause for the rise and fall of electrolyte level. The change in hydroxide ion and water concentration in the positive and negative plate compartments and the direction of electrolyte level change are detailed in Table VII for charge and discharge conditions in the three electrochemical systems.

The osmotic effects in cells with cellophane create a significant rise in electrolyte level in the negative plate compartment on charge and a corresponding <u>decrease</u> in level in the positive plate compartment. The effect on continuous cycling is to make the cell positive plates distinctly electrolyte limited on charge. In silver-cadmium cells, an inverse wrap should change charge limited cells to discharge limited cells and should improve performance characteristics in orbits where charging the cell is the more difficult operation.

The introduction of a bellows device in a Ag-Cd or Ag-Zn cell will be more complicated because of the osmotic effect.

3.2 Normal Variation of Electrolyte Level in Ag-Cd Cells. - To obtain a measure of the normal fluctuation of electrolyte during charging and discharge, 12 sealed ESB SSC-15 Ag-Cd cells were charged at a constant current of 0.70 amps (10 ma/in²) to a voltage cutoff of 1.55 volts for the limiting cell of twelve. Electrolyte levels were observed in inches from the top of the plates during the 18 hour charge. Figure 3 shows the average variation in electrolyte level from the 70% fully discharged state to the fully charged state and the effect of the separator system. All cells had the semi-permeable membrane in "U" fold wrap on the positive plates. The net electrolyte level changes during charge are given in Table VIII.

The cells were then discharged at the 7.5 ampere rate to 0.6 V, delivering 16.9 AH. During the 2.25 hour discharge and for 6 hours thereafter, electrolyte levels were monitored. The electrolyte level changes during discharge and the net change observed 6 hours later are tabulated in Table VIII.

Electrolyte levels do fall during discharge and rise during charge, but the degree is dependent upon the separator system and the method of wrap. Level changes occurring through fibrous sausage casing are less than expected because back flow to counteract concentration changes created during discharge almost keeps pace with the discharge. Level changes through cellophane occur almost exponentially with discharge time and are partially corrected over a 6 hour period after discharge is terminated. Any bellows design to be incorporated in Ag-Cd cells must account for the rise and fall of electrolyte due to osmotic effects created by changing KOH and water concentrations during charge and discharge.

3.3 Proposed Design for Ag-Cd Cells with Bellows. - Data at MBD has shown that Ag-Cd cells must operate with much more electrolyte per cell than required for nickel-cadmium cells. Continuing hydrolysis of the cellulosic semi-permeable membranes consumes electrolyte to the extent that a cell marginal in electrolyte content when a cycling routine is initiated will become definitely electrolyte limited during cycle life.

Semi-permeable membranes effectively stop the macro transfer of 0_2 gas from positive to negative plates through pores in the separator system except for a portion of the oxygen dissolved in the electrolyte. The need for a very dry state in the cell does not exist provided the recombination of 0_2 generated at the AgO plates during overcharge can be consumed by oxygen electrodes. (10) ESB, therefore, proposes

that the Ag-Cd bellows test cells to be fabricated on this contract utilize ESB oxygen electrodes connected to the main negative plates as the means for creating the rapid $\mathbf{0}_2$ recombination essential to feasible bellows operation. The first cells of this type using metal bellows or plastic pillows will be manufactured during the next quarter.

An alternate recombination technique is being investigated by Charkey and Dalin (11). Progress on Contract NASS-3452 will be watched closely for possible application of recombination techniques other than oxygen electrodes to bellows cells.

4. <u>New Technology</u>. - The proposed substitution of plastic pillows for metal bellows in sealed cells to control electrolyte levels is believed to be new technology. Fabrication of the pillows follows standard heat sealing procedures common in the plastics industry.

5. Program for Next Quarter. -

- 5.1 <u>Task l.</u> Fabricate fifteen 6-ampere-hour Ni-Cd sealed test cells in Lucite jars with pressure gauges and modifications of bellows, plastic pillows, and cell pack separator systems to initiate cycling tests on realistic satellite orbits.
- 5.2 <u>Task 2.</u> Design and fabricate six 12-ampere-hour sealed Ag-Cd test cells with oxygen electrodes to increase recombination rates and plastic pillows as electrolyte control devices for cycling tests to demonstrate feasibility of bellows idea in the Cd/KOH/AgO system.

5.3 <u>Task 3.</u> - Select and procure optimum metal bellows with self-contained pressure actuated electrical switch for installation in a sealed Ni-Cd cell to terminate overcharge at a preset high cell pressure and to turn on charger as soon as cell pressure has dropped to a preset value.

6. Conclusions and Recommendations. -

- 6.1 Control of electrolyte level in sealed 4.0 AH sintered plate Ni-Cd cells by partially inflated sealed plastic pillows has been demonstrated.
- 6.2 The plastic pillows, essentially a bellows device, are compressed during the high cell pressures created during overcharge, allowing the electrolyte level in the cell to fall below the bottom of the plates. The increased exposed negative plate area reduces gas pressures during discharge and on open-circuit by increasing recombination rates. A high electrolyte level is restored as the plastic pillows expand forcing electrolyte back into the cell pack.
- 6.3 A survey of commercially available metal bellows was made for the sealed cell application. At this time plastic pillows appear to offer the same ΔV volume change desired in one-half the installed volume required for metal bellows.
- 6.4 A prime problem area will be the selection of separator and electrolyte volume which will not over-wet negative plates even when the plate pack is fully drained and thus prevent rapid recombination

during discharge, open-circuit, and the early portions of recharge.

6.5 Preliminary cell tests on sealed Ag-Cd cells have shown a rise in electrolyte level in the negative plate compartment during charge, a fall during discharge, and the opposite level changes in positive plate compartments, probably the result of osmotic pressures created across the semi-permeable cellophane separator membrane by concentration changes. Bellows designs in Ag-Cd cells will be required to counteract such osmotic effects.

BIBLIOGRAPHY

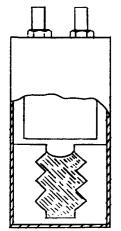
- 1. Contract NASS-3813.
- U. S. Patent 2,131,592, 27 September 1938, A. E.
 Lange et al.
- 3. U. S. Patent 2,614,138, 14 October 1952, P. A. C. Jacquier.
- 4. J. C. Cooper and A. Fleischer, Screening Methods for Separators for Alkaline Silver-Oxide Zinc Secondary Batteries, August 1964.
- 5. Final Report, Contract NASS-1045, Research and Development Program on Sealed Nickel-Cadmium Cells for Space Use, April 30, 1963.
- D. B. Colbeck and A. M. Chreitzberg, Development of Sealed Low Rate Silver-Oxide-Zinc Cells, Second Quarterly Progress Report, May 22, 1962.
- 7. D. H. Collins, Batteries, Pergamon Press, 1963, Page 122.
- 8. Dehmelt, K. and von Dohren, H. Proc. Annual Power Sources Conference, 13th 1959, PP 85-89.
- Seiger, H. N., 4th Quarterly Progress Report, Signal Corps Contract No. DA36-030, SC85390, 1 April 1961 -30 June 1961.

(Continued)

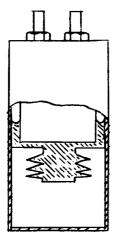
- 10. W. N. Carson et al, Final Project Report, Contract NASS-2817, June 1963.
- 11. A. Charkey and G. A. Dalin, Second Quarterly Progress Report, Contract No. NASS-3452, 31 December 1963.

FIGURE 1

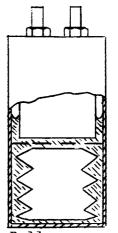
TYPICAL BELLOWS INSTALLATIONS IN SEALED CELLS



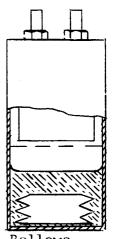
Bellows Extended In Overcharge



Bellows Collapsed After Discharge

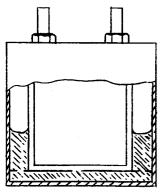


Bellows Extended After Discharge

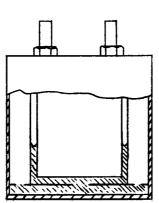


Bellows Collapsed In Overcharge

A Internal Actuation

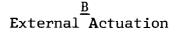


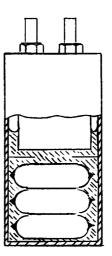
Air Space Compressed In Overcharge



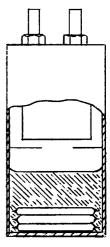
Air Expanded After Discharge

Bellows Replaced by Air Chamber





Pillows Expanded After Discharge



Pillows Compressed During Overcharge

<u>D</u>
Bellows Replaced By
Partially Inflated
Pillows

EXPERIMENTAL NICKEL-CADMIUM CELL 6.0 AH PLATE GROUPS

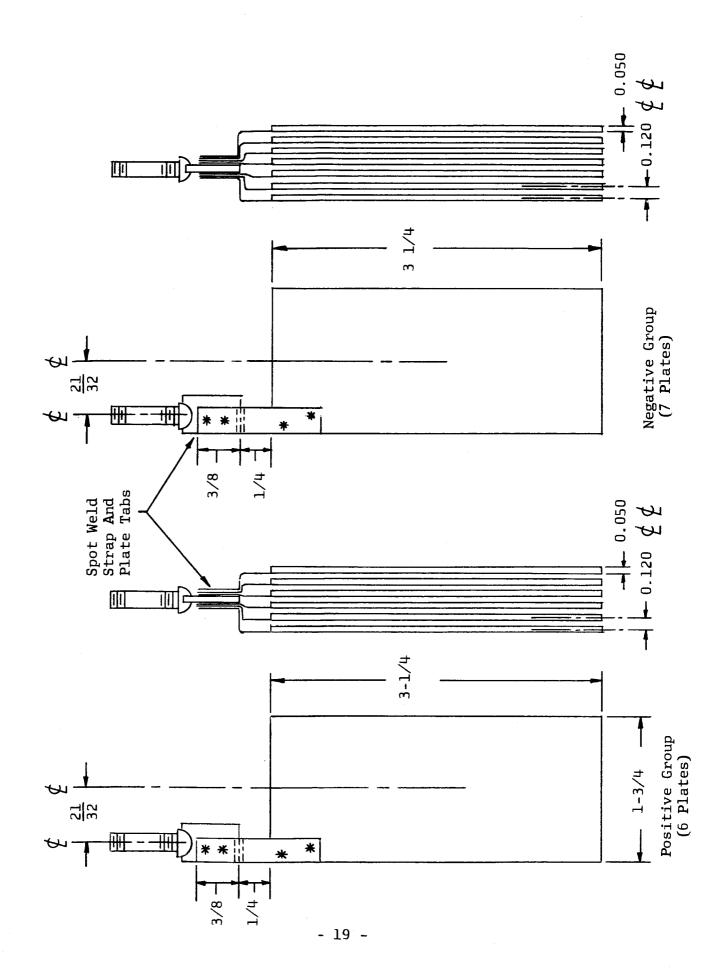


Figure 3

ELECTROLYTE LEVEL VARIATION
DURING CHARGE OF SEALED 15 AH
Ag-Cd CELLS

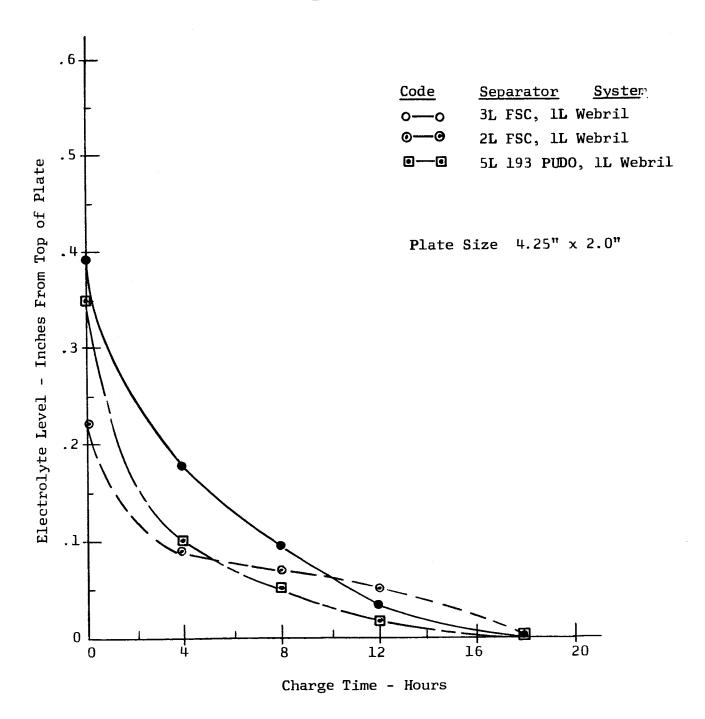


TABLE I

EFFECT OF ELECTROLYTE CONTENT ON 2-HOUR RATE CAPACITY OF SINTERED PLATE NICKEL CADMIUM CELL WITH MICROPOROUS PVC SEPARATORS

Rated Capacity = 4 AH

Element Composition = 4 positive plates @ 1-3/4" X 3-1/4" X .050"

5 negative plates @ 1-3/4" X 3-1/4" X .050"

8 separators = Pormax (microporous sheet)

2 X 3-1/2" X .012"

Test Condition:

Charge: to 1.4C at C/10 (Input = 5.6 AH) (Charge 14 hrs. at 400 mA)

Open Circuit Stand: 1 to 3 hours

Discharge: at C/2 to 1.00 V (2 amp)

Electrolyte Composition: 31% KOH

	DISCHARGE CAPACITY IN AMPERE-HOURS						
Test		CEL	L ELECTROLYTE (CONTENT			
Cell	Forced Drain	Simple Drain	1/3 Level	2/3 Level	Full To Plate Top		
No.	39 Grams*	42 Grams	50 Grams	63 Grams	77 Grams		
1.	4.44 <u>Average</u> : 4.58 4.62 4.58 4.68	4.20 <u>Average</u> : 4.44 4.56 4.40	4.20 <u>Average</u> : 4.44 4.32	4.14 <u>Average</u> : 4.34 4.24	4.50		
2	3.60 <u>Average</u> : 4.16 4.22 4.08 4.32	3.60 <u>Average</u> : 3.70 3.88 3.73	3.64 <u>Average</u> : 3.70 3.67	3.46 <u>Average</u> : 3.74 3.60	3.80		

^{(*) 26.5%} of weight of dry element.

TABLE II

RELATIVE CAPILLARY PROPERTIES

OF SEPARATOR MATERIALS

			Materials Tested			
			Plastic	Nylon	Pormax	Pellon
Capil.	lary		Screen	Cloth	PVC	2506K
Prope:	rty	Unit	18x14 Mesh	116x116 Mesh	Microporous	Felt
	y and Wet ickness	mils	19	3.5	10	11-13
	sorbency l By Weight	grams 31% KOH gram dry separator	.003	1.1-1.4	3.5-3.8	5.4-5.6
2.7	2 By Volume	mg 31% KOH in ² -mil wet separator	.01	3.0-4.0	13-15	14-15
i i	cking Height At 1 "g" at mes: 1.5 hrs. 7.0	inches			0.5 0.8	4.1 5.8
	16.0 35.0		0	0	1.0 1.5	6.8 7.0

TABLE III
SEPARATOR DRAIN TESTS

		Electrolyte Loss and Retention After 2 Minutes Simple Drainage				
		Loss		Retention		
	Dry	Weight				
Separator	Thickness	% of Original	9	9		
Material	(mils)	Flooded Vol.*	cc/in ²	cc/in ²		
Pormax	12	0	0	0.136		
Pormax + Filament	23.5	47.5%	0.163	0.180		
9 XX Nylon (2 layers)	7	40.5%	0.078	0.115		
9 XX Nylon (2 layers) + Filament	18	72.8%	0.320	0.119		
Glass-Plastic Screen- Long Axis Vertical	19	63.7%	0.193	0.110		
Glass-Plastic Screen- Long Axis Horizontal	19	69.8%	0.207	0.090		
Saran Screen-Loops Vertical	17.5	69.4%	0.260	0.115		
Saran Screen-Loops Horizontal	17.5	66.7%	0.234	0.117		
Polyethylene Net	43	91.3%	0.731	0.069		

- (*) Test Procedure:
- (a) Mount 1.0" x 3.5" sample specimen (one layer) between Lucite plates.
- (b) Saturate in horizontal position with 31% KOH.
- (c) Erect assembly quickly to vertical position and drain for 2.0 minutes.
- (d) Weigh drained assembly and compare to saturated weight before drain.

TABLE IV CHARACTERISTICS AND ESTIMATED PERFORMANCE OF COMMERCIAL METAL BELLOWS

		Bel	lows Cha	aracteri	stics
	Bellows Description			Length*	
Supplier	Derrows Description	Туре	△ V / V*	Inches	Remarks
Metal Bellows Corp., Sharon, Mass. Welded diaphragm types available in four basic contours: Flat plate, nesting ripple, single sweep and torus; both "off-the-shelf" and special types are supplied. Material: stainless steels. Nesting ripple contour off-the-shelf bellows type 347 stainless steel.			0.278	4.14	Compres- sion
	P/N A-20115 modified for action from nested state.	Mod.	0.312	3.69	Extension
	Calc'd nesting ripple bellows of AM350 steel for action from completely nested state.	Cale'd	0.364	3.36	Extension
National Bellows Co. Stratford, Conn. (Div. of Van Allen- Andrews, Inc.)	Welded diaphragm flat plate type in stainless steel. 1200 standard bellows are listed in catalog.	P/N 3401	0.237	5.15	Compres- sion
Robertshaw-Fulton Controls Co., Knoxville, Tenn.	Hydraulically formed single ply stainless steel bellows.	Ref. #358	0.217	5.48	Compres- sion
Servometer Corp., Clifton, N.J.	Miniature nickel bellows of electrodeposited type. No. stock bellows. Max. length 3 1/2". Rectangular shapes can be made. 0.0. Range: 0.063 to 1.25" Bellows calc. from listed	Max. PSI For Max. Stroke			
	data Bellows calc. from listed	34	0.247	4.97	Compres- sion
	data	134	0.125	9.76	Compres- sion
· · · · · · · · · · · · · · · · · · ·	Bellows calc. from listed data	77	0.174	7.06	Compres- sion

 ^(*) Maximum volume change per square chamber volume.
 (**) Length of 1" diameter bellows for a 20 cc volume change.

TABLE IV

CHARACTERISTICS AND ESTIMATED PERFORMANCE OF COMMERCIAL METAL BELLOWS (Continued)

	and the second s	Ве	llows	Charac	teristics
Supplier	Bellows Description	Туре	∆v ⁄v	Length Inches	
Miniflex Corporation, Lawndale, Calif.	Miniature stainless steel bellows, on the shelf item. 0.D. Range: 0.226 to 1.270		0.144	8.29	Compression
Keller Products Co., Hanover, N.J.	Welded diaphragm nickel and stainless steel bellows in four contours including	BEB-160- 7500	0.110	11.1	Compression
"nesting types".		BEB-160- 6103	0.012	98.6	Compression
U.S. Flexible Tubing Co., Bartlett, Ill.	Stainless steel bellows	1/2 X 3/4	0.160	11.6	Compression
B.F. Goodrich Co., Aerospace and Defense Products Div. Akron, Ohio	Omega design seamless bellows. No stock items. Hydraulic and mechanical processes. O.D. range: 1/4" to 1 1/2" Stainless steel bellows-switch ass'y B.F.G. Dwg. C3K1060	3K-1060	0.037	32.8	A bellows ass'y minus the switch will show improved values.

TABLE V ELECTROLYTE LEVEL VARIATION IN 4 AH Ni-Cd CELL CONTAINING POLYETHYLENE PILLOWS WITH EXTERNALLY IMPOSED PRESSURE CHANGES

		T		Electr	olyte Level	.s*		
1		Free Electrolyte Volume						
	_		5 cc		0 cc		55 cc	
Impos		mm B elow	% P late	mm B elow	% P late	mm Delles	% D1	
Press Gauge	Ab solute	Tops	Immersion	Tops	Immersion	Below Tops	Plate Immersion	
20" Hg Vac	4.8 PSI	10	87.9			9 above	Flooded	
15" Hg V a c	7.3 PSI	33	5 9. 8			i ļ	95.1	
10" Hg V a c	9.8 PSI	51	3 7.8			23 .	72.0	
4" Hg V a c	12. 7 PSI	6 3	23.2			33	59.8	
0	14.7 PSI	6 9	15.9	5 3	35.4	40	51.2	
1 5 P S IG	2 9.7 P S I	87	5mm Below Bottoms	76	7.3	59	28.1	
30 PSIG	44.7 PSI	88	6mm Below Bottoms	82	Exactly at Plate Bottoms	64	22.0	
45 PSIG	59.7 PSI	89	7mm Below Bottoms	87	5mm Below Bottoms	67	18.3	
5 0 PSIG	6 4. 7 P S I	90	8mm Below Bottoms	88	6mm Below Bottoms	68	17.1	

(*) Separator: Single layer of 9XX nylon cloth. Electrolyte: 31% KOH.

TABLE VI

ELECTROLYTE LEVEL VARIATION DURING CHARGE AND OPEN-CIRCUIT
OF 4 A.H. CELL WITH DOUBLE NYLON CLOTH SEPARATORS AND PILLOWS

	Time		Electrolyte	Level
Cell	Elapsed	Cell	Distance Below	%
Function	Hrs.	Pressure-Atm	Plate Tops mm	Immersion
Open-Circuit	Start	0.06	21	74.4
		·		
C/10 Charge	9.5	0.47	62	24.4
	10.5	0.60	68	17.1
	11.0	0.67	69	15.9
	14.0	1.20	82	0
Open-Circuit	2	0.83	74	9.8
	3.2	0.63	70	14.6
	4	0.53	64	22.0
	5	0.43	59	28.0
j .	22.7	0.13	26	68.3
	29	0.11	24	70.8
Continued				
C/10 Overcharge	15.5	3.18	Below Bottoms	0
Open-Circuit	0.3	3.00	Below Bottoms	0
	0.5	2.90	Below Bottoms	0
· ·	0.7	2.80	Below Bottoms	0
	1	2.53	Below Bottoms	0
	2	1.95	Below Bottoms	0
	3	1.54	Below Bottoms	0
	4.8	1.00		pro-Cité
	6	0.82	₩.	
	10.5	0.40		
•	14.5	0.26		
	20.5	0.23		
	23	0.20	39	52.5
	120	0.06	21	74.4
0.420.03				
C/10 Charge after		1.00	79	3.7
discharge at		1.24	82	At Bottoms
the C/2 Rate		1.37	83	Below Bottoms
	13.0	1.65	84	Below Bottoms
	14.0	1.95	Pers 1800	Below Bottoms
		<u> </u>		

TABLE VII CONCENTRATION AND LEVEL CHANGES IN ELECTROLYTE DURING CHARGE AND DISCHARGE*

Reaction in Positive	Reaction in Negative	Net Change in El	ectrolvte Level
Plate Compartment	Plate Compartment	Positive	Negative
During Charge	During Charge	Compartment	Compartment
System: Cd/KOH/NiOOH			
On Nickelic Oxide Plates:	On Cadmium Plates:	No change.	No Change.
	**	Ũ	
$2 \text{ Ni (OH)}_2 + 20\overline{\text{H}} \longrightarrow$	Cd0 + H ₂ 0 + 2e>	No membrane	No membrane
	2	to create	to create
2 NiOOH + 2H ₂ O + 2e	Cd + 20H	osmotic	osmotic
-		effect.	effect.
F -7	c -		
OH falls during charge.	OH rises during		
	charge.		
HOH rises during charge.	HOH falls during		
	└		
System: Cd/KOH/AgO			
On AgO Plates:	On Cadmium Plates:	Membrane	Membrane
	I.	present.	present.
Ag + 20H →	Cd0 + H ₂ 0 + 2e>	_	
	_		
Ag0 + H ₂ 0 + 2e	Cd + 20H	Water trans-	Water trans-
_		ferred out.	ferred in.
		<u>Electrolyte</u>	Electrolyte
1	r -	<u>level falls</u> .	level rises.
OH falls during charge.	OH rises during		
	charge.		
HOH rises during charge.	HOH falls during		
	charge.		
System: Zn/KOH/AgO			
On AgO Plates:	On Zinc Plates:	Membrane	Membrane
_		present.	present.
Ag + 20H>	$Zn0 + H_20 + 2e \longrightarrow$		
	_		
AgO + H ₂ O + 2e	Zn + 20H	Water trans-	Water trans-
		ferred out.	ferred in.
		<u>Electrolyte</u>	<u>Electrolyte</u>
F7		<u>level falls</u> .	level rises.
OH falls during charge.	OH rises during		
- -	charge.		
HOH rises during charge.	HOH falls during		
	charge.	<u> </u>	

(*)

All processes shown are reversed during discharge. Cd (OH) $_2$ is a preferred reactant. Reaction written to show consumption of $\rm H_2O_{\bullet}$ (**)

TABLE VIII

ELECTROLYTE LEVEL CHANGES IN SEALED Ag-Cd CELLS
DURING CHARGE AND DISCHARGE

Operation	Semi-Permeable Membrane	Thickness, Dry	Inches Wet	Mean Electrolyte Level Change, Inches
Charge after 70%	2L FSC	.006	.0156	0.22*
Discharge at C/20 Rate	3L FSC	.009	.0234	0.39
	5L 193 PUDO	.0045	.0149	0.35
Discharge at C/2 Rate		Mean Electrolyte Lev During 2.25 Hour Discharge		el Change, Inches Net Change After 6 Hrs.Stand
	2L FSC	-0.25		-0.17
	3L FSC	-0.11		-0.15
	5L 193 PUDO	-1.60		-0.51

^(*) Mean value of 3 cells each containing fibrous sausage casing and 6 cells containing 5L 193 PUDO cellophane.